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Abstract of JP11021552

PROBLEM TO BE SOLVED: To provide a phosphorescent phosphor which not only has long afterglow time and high afterglow brightness, but also can be used for obtaining a wide variety of gradations of color, and further for producing an article of such a complicated form that is difficult to manufacture from a conventional aluminate phosphor. **SOLUTION:** This phosphorescent phosphor is activated by a divalent europium and the chemical composition is represented by the formula: R_{0.1}a(Al_{1-x}Ga_x)₂O₃.b(Si_{1-y}Gey)O₂.cEu<2+>.dM<a+>, wherein R is at least one member selected from the group consisting of alkaline earth metals such as Ba, Sr, Ca, Mg and the like and Zn, and M is a coactivator and at least one member selected from the group consisting of Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, a, b, c, d, e, x and y being in ranges of 0.3<=a<=8.0, 0.01<=b<=2.0, 0.01<=c<=0.3, 0.001<=d<=0.3, 0<=x<1.0, 0<=y<=1.0, respectively. A phosphorescent glass ceramics containing this phosphor is also provided.

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(54)【発明の名称】 蓄光性蛍光体

(57)【要約】

【課題】 長残光時間・高残光輝度であり、更に多様な色調の発光色が得られ、従来のアルミニン酸塩蛍光体では製造が困難な形状の物品をも製造することが可能な、蓄光性蛍光体を提供する。

【解決手段】 2価のユーロビウムで賦活され、その化学組成式は $R_2O \cdot a(A_{1-x}Ga_x)_2O_4 \cdot b(S_{1-y}Ge_y)_2O_4 \cdot cEu^{2+} \cdot dM^{3+}$ (但し、RはBa, Sr, Ca, Mg等のアルカリ土類金属およびZnからなる群から選ばれる少なくとも1種であり、Mは共賦活剤で、Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Luからなる群から選ばれる少なくとも1種である)で示され、a, b, c, d, x, yはそれぞれ $0.3 \leq a \leq 8$, $0.001 \leq b \leq 2$, $0.001 \leq c \leq 0.3$, $0.001 \leq d \leq 0.3$, $0 \leq x < 1.0$, $0 \leq y \leq 1.0$ の範囲にあることを特徴とする蓄光性蛍光体およびこれを含むことを特徴とする、蓄光性蛍光ガラスセラミックスを得る。

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【特許請求の範囲】

【請求項1】 2価のユーロピウムで賦活され、その化学組成式は $RO \cdot a (Al_{1-x} Ga_x) \cdot O \cdot b (Si_{1-y} Ge_y) O \cdot c Eu^{2+} \cdot d M^{+}$ （但し、RはBa, Sr, Ca, Mg等のアルカリ土類金属およびZnからなる群から選ばれる少なくとも1種であり、Mは共賦活剤で、Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Luからなる群から選ばれる少なくとも1種である）で示され、a, b, c, d, x, yはそれぞれ
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0.3 ≤ a ≤ 8,
0.001 ≤ b ≤ 2,
0.001 ≤ c ≤ 0.3,
0.001 ≤ d ≤ 0.3,
0 ≤ x < 1.0,
0 ≤ y ≤ 1.0 の範囲にあることを特徴とする蓄光性蛍光体。

【請求項2】 請求項1に記載の蓄光性蛍光結晶を含むことを特徴とする、蓄光性蛍光ガラスセラミックス。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は化学組成式 $RO \cdot a (Al_{1-x} Ga_x) \cdot O \cdot b (Si_{1-y} Ge_y) O \cdot c Eu^{2+} \cdot d M^{+}$ （但し、RはBa, Sr, Ca, Mg等のアルカリ土類金属およびZnからなる群から選ばれる少なくとも1種であり、Mは共賦活剤で、Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Luからなる群から選ばれる少なくとも1種である）で示され、長残光時間・高残光輝度で、発光波長の多様な、新規な蓄光性蛍光体及びこれを含んだガラスセラミックスに関するものである。

【0002】

【従来の技術】 蛍光は物質が外部からの刺激（励起）によって可視域付近の光を発する現象であり、蛍光灯・放電ランプ・CRT (Cathode Ray Tube)いわゆるブラウン管等の発光がこれである。蛍光を発する物質を蛍光体というが、励起停止後に目に感じられる程度の時間（0.1秒程度）の蛍光が続く場合、これを撲光と呼ぶ。また、撲光の続く時間、すなわち残光時間が室温で数時間に及ぶような長残光性を持つ蛍光体を、蓄光性蛍光体と呼んでいる。蓄光性蛍光体に関しては、これまでにZnS : Cuに代表される硫化物と、RAI_{1-x}O_x (R : アルカリ土類金属)を母結晶とした酸化物の二種類が報告されている。ZnS : Cu硫化物蓄光性蛍光体は数十年前に実用化されたが、残光時間はせいぜい3時間程度で短いという問題点がある。また、この蓄光性蛍光体は日光に含まれる紫外線ならびに、大気中に含まれる水分により、 $ZnS + H_2O \rightarrow Zn + H_2S$ なる分解反応が生じて、粒子自体が黒化し、残光輝度が徐々に低下し、短期

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間で残光機能が著しく低下するという致命な欠点を持っている。そのため、この種の蓄光性蛍光体は主に夜光時計や屋内の夜間表示等、非常に限られた用途に限定されていた。一方、最近開発された、RAI_{1-x}O_xを母結晶としてEu²⁺で賦活されたアルミニン酸塩蓄光性蛍光体（米国特許第5376303号、米国特許第5424006号、特開平8-73845号、特開平8-127772号、特開平8-151573号、特開平8-151574号）は残光時間がZnS : Cuより長く、しかも化学耐久性と耐光性にも優れるという特性を持ち合わせているため、既存の夜光時計や屋内の夜間表示等の用途に加えて、防災標識・位置認識用危険防止の表示・装飾品等の幅広い用途が期待される。

【0003】

【発明が解決しようとする課題】 蓄光性蛍光体の応用分野が拡大するにつれて、残光輝度と残光時間のさらなる向上が望まれる。

【0004】 また、蓄光性蛍光体を看板等の装飾品用に使用する場合は、できるだけ多様な色調の残光を使用することが望ましい。上記特開平8-151573号には、アルミニン酸塩蛍光体と賦活剤、共賦活剤の組み合わせにより色調を変化させることができることが開示されているが、色調の変化のために使用可能な共賦活剤の種類は限定されており、したがって得られる色調の変化も比較的狭い範囲に限られている。

【0005】 さらに、蓄光性蛍光体を装飾品等に使用する場合、例えば厚さ1mm以下の肉薄のチューブの形状に成形することは、焼結体からなる従来のアルミニン酸塩蓄光性蛍光体では極めて困難であり、この難点を解決した蓄光性蛍光体を提供することが望まれる。

【0006】 本発明は、前記従来のアルミニン酸塩蓄光性蛍光体が有する問題点にかんがみてなされたものであり、従来のものよりも長残光時間・高残光輝度を実現しながら、発光色においてより多様な色調の変化を得ることができる新規な蓄光性蛍光体を提供しようとするものである。また、本発明は、アルミニン酸塩蓄光性蛍光体を使用しては製造することが困難な形状の物品を製造することが可能な、新規な蓄光性蛍光体を提供しようとするものである。

【0007】

【課題を解決するための手段】 上記課題の解決のため、本発明は賦活剤としてのEu²⁺と共に共賦活剤を同時にドープした、化学組成式は $RO \cdot a (Al_{1-x} Ga_x) \cdot O \cdot b (Si_{1-y} Ge_y) O \cdot c Eu^{2+} \cdot d M^{+}$ （但し、RはBa, Sr, Ca, Mg等のアルカリ土類金属およびZnからなる群から選ばれる少なくとも1種であり、Mは共賦活剤で、Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Luからなる群から選ばれる少なくとも1種である）で表される結晶及びこれを含んだガラス

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セラミックスからなる新規な蓄光性蛍光体を提供する。【0008】これまでにEu²⁺を賦活剤としたアルカリ土類金属アルミニウム珪酸塩において、数多くの蛍光体が開発されている。例えば、特公昭47-41には、R₂O₃·Al₂O₃·2SiO₂·Eu (R: アルカリ土類金属) からなる蛍光体が示され、特公平7-45656には、(Ba,Ca,Mg,Eu_x)O₃·aAl₂O₃·bSiO₂からなる蛍光体が示されている。これらの蛍光体はケイ素を含まないアルミニ酸塩蛍光体とは異なった発光特性を示している。これはホストの配位子場の違いに起因しているものと考えられる。なぜなら、Eu²⁺の発光は4f⁷-4f⁶5d遷移を利用していているため、Eu²⁺のまわりの化学環境、すなわちEu²⁺を取り込むホストの配位子場の強さの影響を非常に受けやすいからである。これらのアルカリ土類金属アルミニウム珪酸塩蛍光体は、実用に必要とされる十分な発光輝度を有するが、全て蛍光灯やCRT用に開発されたもので、残光時間が非常に短い。実際に特公昭47-41に示されたRO·Al₂O₃·2SiO₂·Eu 蛍光体の場合、残光時間は著しく短く、時定数は1マイクロセカンド以下であると記載されている。すなわち、これらの材料は光を照射する時に発光するが、照射をやめると発光が素早く減衰し、残光性を有しない蛍光体である。

【0009】ここで、配位酸化物イオンの電子密度、すなわち塩基度が高いほど配位子場は強く、5d軌道の分裂が大きくなり、発光開始準位エネルギーが下がるため、塩基度の増加に伴って蛍光は長波長側にシフトすることが知られている。そこで、従来の残光性を有しない蛍光体として蛍光灯やCRT用に使用されてきたアルカリ土類金属アルミニウム珪酸塩蛍光体に対して、残光時間を長くするために有効である共賦活剤を添加することによって長残光性を実現すれば、塩基度が相互に異なるAl₂O₃+Ga₂O₃とSiO₂+GeO₂の比を調整することにより、ホストの配位子場の強さを幅広く変えることが可能となるので、既存のアルミニ酸塩蓄光性蛍光体よりも一段と変化に富む発光特性を得ることが期待できる。またアルカリ土類金属アルミニウム珪酸塩蛍光体は、溶融してガラス化した後、熱処理することにより化学組成式はRO·a(Al_{1-x}Ga_x)₂O₃·b(Si_{1-y}Ge_y)O₂·cEu²⁺·dMⁿ⁺ (但し、RはBa、Sr、Ca、Mg等のアルカリ土類金属およびZnからなる群から選ばれる少なくとも1種であり、Mは共賦活剤で、Nb、Zr、Bi、Mn、Sn、La、Ce、Pr、Nd、Sm、Gd、Tb、Dy、Ho、Er、Tm、Yb、Luからなる群から選ばれる少なくとも1種である)で示され、a、b、c、d、x、yはそれぞれ0.3≤a≤8、0.001≤b≤2、0.001≤c≤0.3、0.001≤d≤0.3、0≤x<1.0、0≤y≤1.0の範囲にあることを特徴とする蓄光性蛍光体であり、請求項2に記載の発明は、請求項1に記載の蓄光性蛍光結晶を含むことを特徴とする、蓄光性蛍光ガラスセラミックスである。

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【0010】本発明者は前記のような着想に基づいて、残光特性のないアルカリ土類金属アルミニウム珪酸塩蛍光体に注目し、研究を重ねた結果、賦活剤としてのEu²⁺および共賦活剤を導入すると共に、Al₂O₃+Ga₂O₃とSiO₂+GeO₂の組成比および、Eu²⁺の濃度ならびに共賦活剤の濃度をそれぞれ特定の範囲内で選択組み合わせることにより、従来のアルミニ酸塩蓄光性蛍光体に比べてより多彩な発光特性を有し、長残光時間・高残光輝度で、発光波長が従来よりも多様化させることができ、しかもガラスセラミックスに成形することも可能な蓄光性蛍光体を見いだし、本発明をなすに至った。

【0011】すなわち、請求項1に記載の蓄光性蛍光体は、化学組成式RO·a(Al_{1-x}Ga_x)₂O₃·b(Si_{1-y}Ge_y)O₂·cEu²⁺·dMⁿ⁺ (但し、RはBa、Sr、Ca、Mg等のアルカリ土類金属およびZnからなる群から選ばれる少なくとも1種であり、Mは共賦活剤で、Nb、Zr、Bi、Mn、Sn、La、Ce、Pr、Nd、Sm、Gd、Tb、Dy、Ho、Er、Tm、Yb、Luからなる群から選ばれる少なくとも1種である)で示され、a、b、c、d、x、yはそれぞれ0.3≤a≤8、0.001≤b≤2、0.001≤c≤0.3、0.001≤d≤0.3、0≤x<1.0、0≤y≤1.0の範囲にあることを特徴とする蓄光性蛍光体であり、請求項2に記載の発明は、請求項1に記載の蓄光性蛍光結晶を含むことを特徴とする、蓄光性蛍光ガラスセラミックスである。

【0012】本発明の蓄光性蛍光体において、aはAl₂O₃、またはAl₂O₃およびGa₂O₃の組成比を、bはSiO₂および/またはGeO₂の組成比を示すものである。aとbはそれ自身で互いに影響しあうものであり、それらを調整することによってホストの配位子場の強さが変化し、その結果、発光波長、残光輝度および残光時間も変わる。aを小さくし、bを大きくすれば、あるいはaを大きくし、bを小さくすれば残光輝度を高くすることができます。しかし、その範囲には限界があり、0.3≤a≤8の範囲において、b<0.001ではSiおよび/またはGeの効果が弱く、b>2でも残光輝度の高い蛍光体を得ることができない。また、0.001≤b≤2の範囲において、0.3≤a≤8以外の範囲においても、残光輝度の高い蛍光体を得ることはできない。好ましくは、0.3≤a≤6および0.001≤b≤2の範囲、特に好ましくは、0.5≤a≤3および0.002≤b≤2の範囲である。

【0013】cは賦活剤の濃度を示すもので、0.001≤c≤0.3の範囲でなければならない。c<0.001では光吸収が悪く肉眼で認識できるほどの残光輝度が得られず、逆にc>0.3では濃度消光を起こし、残光輝度が低下する。好ましくは、0.001≤c≤0.2、特に好ましくは、0.002≤c≤0.1の範囲である。

【0014】dは共賦活剤の濃度を示すもので、 $0.01 \leq d \leq 0.3$ の範囲である。d < 0.001では残光時間と残光輝度への効果が弱く、逆にd > 0.3では残光輝度が次第に低下する。好ましくは、 $0.001 \leq d \leq 0.2$ 、特に好ましくは $0.002 \leq d \leq 0.15$ の範囲である。

【0015】xはAlをGaで置換するときの置換率を示すもので、Alの一部をGaに置換することによっても、残光時間・残光輝度において、従来のZnS:Cuよりも優れた蛍光体を実現できる。尚、AlのGaによる置換はほぼ100%の置換も可能であるが、より良好な前記特性を得ようとするならば、 $x \leq 0.5$ の範囲が好ましく、特に好ましくは $x \leq 0.2$ の範囲である。

【0016】yはSiをGeで置換するときの置換率を示すもので、Siの一部をGeに置換することによっても、残光時間・残光輝度において、従来のZnS:Cuよりも優れた蛍光体を実現できる。尚、SiのGeによる置換は全置換も可能であるが、より良好な前記特性を得ようとするならば、 $y \leq 0.5$ の範囲が好ましく、特に好ましくは $y \leq 0.2$ の範囲である。

【0017】また、本発明の蓄光性蛍光体の合成の際に、フランクスとして硼酸、Li₂CO₃、LiCl₁、リン系化合物等を添加することができる。その最適な添加量はm o 1%で0.05~8%の範囲である。

【0018】

【発明の実施の形態】本発明の蓄光性蛍光体は以下の焼結法で合成することができる。本発明の蓄光性蛍光体の構成成分である酸化物、もしくは熱分解によって酸化物となり得る各種化合物を、所定の比で秤量し十分に混合した後、アルミナるつぼに入れて還元雰囲気で1100~1600°Cで1~10時間焼成する。組成によっては、得られた焼成物を粉碎し、再度同じ条件で焼成することもある。

【0019】また、本発明の蓄光性蛍光体は、次に述べるガラスセラミックスの製造方法によっても作製できる。すなわち、出発原料を所定の比で秤量し十分に混合した後、アルミナるつぼに入れて還元雰囲気で1300~1600°Cで1~3時間加熱溶融する。その後、溶融液を鉄板上にキャストし、板状のガラスを作製する。こうして得られたガラスを、還元雰囲気で950~1250°Cで1~12時間熱処理することによって、化学組成式RO·a(Al_{1-x}Ga_x)₂O₃·b(Si_{1-y}Ge_y)O₂·cEu²⁺·dM⁺ (但し、RはBa、Sr、Ca、Mg等のアルカリ土類金属およびZnからなる群から選ばれる少なくとも1種であり、Mは共賦活剤で、Nb、Zr、Bi、Mn、Sn、La、Ce、Pr、Nd、Sm、Gd、Tb、Dy、Ho、Er、Tm、Yb、Luからなる群から選ばれる少なくとも1種である)からなる結晶を含むガラスセラミックス製蓄光性蛍光体が得られる。ガラスセラミックスとすれば、焼結体セラミック

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スでは成形が困難な薄肉のチューブ等の形状をした製品でも、容易に成形することができる。また焼結法によるセラミックスでは、焼結前の粒子間の空隙が焼結体中の空孔として残留してしまい、製品の用途によってはその目的にあった十分な強度が得られない場合があるが、ガラスセラミックスではこのような空孔のない、緻密で均一なものが得られるので、焼結体セラミックスよりも強度において優れる製品が得られる。このようにして焼結法で得られない形のものも実現でき、本発明の蓄光性蛍光体の応用価値がより一層高まる期待される。

【0020】

【実施例】以下、本発明を具体的な実施例により説明するが、本発明はこれら実施例にのみ限定されるものではない。

【0021】

【実施例1】

SrCO ₃	5.69 g
Al ₂ O ₃	3.93 g
SiO ₂	4.63 g
H ₂ BO ₃	0.19 g
Eu ₂ O ₃	0.27 g
Dy ₂ O ₃	0.29 g

上記の配合組成の原料を十分混合し、97N₂+3H₂の混合ガス気流中で1350°Cで2時間焼成し、化学組成式SrO·Al₂O₃·2.00SiO₂·0.04B₂O₃·0.020Eu₂O₃·0.020Dy₂O₃となる蓄光性蛍光体を得た。図1に示すX線回折パターンの解析により、この蓄光性蛍光体はSrAl₂Si₂O₆相からなっていることが明らかになった。図2に励起停止10分後の発光スペクトルを示す。波長420nmと485nm付近にピークを持ち、従来の蓄光性蛍光体に見られない発光特性を有することがわかる。また、目視でも白色の発光が観察され、しかも暗所において24時間以上残光が認識できた。

【0022】

【実施例2】

CaCO ₃	4.42 g
Al(OH) ₃	6.90 g
SiO ₂	5.30 g
H ₂ BO ₃	0.22 g
Eu ₂ O ₃	0.19 g
Nd ₂ O ₃	0.36 g

上記の配合組成の原料を十分混合し、97N₂+3H₂の混合ガス気流中で1350°Cで2時間焼成し、化学組成式CaO·Al₂O₃·2.00SiO₂·0.04B₂O₃·0.012Eu₂O₃·0.024Nd₂O₃となる蓄光性蛍光体を得た。図3に示すX線回折パターンの解析により、この蓄光性蛍光体はCaAl₂Si₂O₆相からなっていることが明らかになった。図4に励起停止10分後の発光スペクトルを示す。発光スペクトルは従来の

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ものと異なって、波長425nm付近の大きな発光ピークと540nm付近の小さな発光ピークからなることがわかる。また、目視で青紫色の発光が観察され、しかも暗所において24時間以上残光が認識できた。

【0023】

【実施例3】

CaCO₃ 4.39g

Al ₂ O ₃	4.27g
Ga ₂ O ₃	0.20g
SiO ₂	4.45g
NH ₄ H ₂ PO ₄	1.76g
Eu ₂ O ₃	0.18g
Nd ₂ O ₃	0.34g

上記の配合組成の原料を十分混合し、97N₂+3H₂の混合ガス気流中で1350°Cで2時間焼成し、化学組成式CaO·0.95Al₂O₃·1.69SiO₂·0.02Ga₂O₃·0.17P₂O₅·0.012Eu₂O₃·0.023Nd₂O₃になる蓄光性蛍光体を得た。このようにして得られた蛍光体はCa-Al-Si-O₃相からなっており、図4に示すような発光特性を有する。また、目視で青紫色の発光が観察され、しかも暗所において24時間以上残光が認識できた。

【0024】

【実施例4】

* CaCO ₃	7.11g
Al ₂ O ₃	7.25g
SiO ₂	0.02g
H ₂ BO ₃	0.18g
Eu ₂ O ₃	0.15g
Nd ₂ O ₃	0.29g

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7.11g	
7.25g	
0.02g	
0.18g	
0.15g	
0.29g	

上記の配合組成の原料を十分混合し、97N₂+3H₂の混合ガス気流中で1350°Cで2時間焼成し、化学組成式CaO·Al₂O₃·0.005SiO₂·0.02B₂O₃·0.006Eu₂O₃·0.012Nd₂O₃となる蓄光性蛍光体を得た。このようにして得られた蛍光体は波長440nmに発光ピークを持ち、目視で青紫色の発光が観察され、しかも暗所において24時間以上残光が認識できた。

【0025】実施例4と同様な方法で、同様な発光色を示す実施例5~10とSiO₂を含まない比較例を作製した。表1は4~10の組成をまとめたものである。図5に励起停止10分後の実施例6と比較例の発光スペクトルを示す。本発明の蓄光性蛍光体はより強く発光することがわかる。また、これらの実施例の蛍光体は暗所において24時間以上残光が認識できた。

【0026】

【表1】

*

実施例	化 学 組 成 式
4	CaO·Al ₂ O ₃ ·0.005 SiO ₂ ·0.02 B ₂ O ₃ ·0.006 Eu ₂ O ₃ ·0.012 Nd ₂ O ₃
5	CaO·Al ₂ O ₃ ·0.009 SiO ₂ ·0.02 B ₂ O ₃ ·0.006 Eu ₂ O ₃ ·0.012 Nd ₂ O ₃
6	CaO·Al ₂ O ₃ ·0.014 SiO ₂ ·0.02 B ₂ O ₃ ·0.006 Eu ₂ O ₃ ·0.012 Nd ₂ O ₃
7	CaO·Al ₂ O ₃ ·0.028 SiO ₂ ·0.02 B ₂ O ₃ ·0.006 Eu ₂ O ₃ ·0.012 Nd ₂ O ₃
8	CaO·Al ₂ O ₃ ·0.036 SiO ₂ ·0.02 B ₂ O ₃ ·0.006 Eu ₂ O ₃ ·0.012 Nd ₂ O ₃
9	CaO·Al ₂ O ₃ ·0.040 SiO ₂ ·0.02 B ₂ O ₃ ·0.006 Eu ₂ O ₃ ·0.012 Nd ₂ O ₃
10	CaO·Al ₂ O ₃ ·0.048 SiO ₂ ·0.02 B ₂ O ₃ ·0.006 Eu ₂ O ₃ ·0.012 Nd ₂ O ₃
比較例	CaO·Al ₂ O ₃ ·0.02 B ₂ O ₃ ·0.006 Eu ₂ O ₃ ·0.012 Nd ₂ O ₃

【0027】また、共賦活剤Ndと共にCe, Pr, Gd, Er, Tm, Luを添加した、実施例11~16及び各実施例に対応した比較例（番号の前に「比較」のついたもの）について、実施例4と同様な方法で作製し、

それらの化学組成式を表2にまとめた。

【0028】

【表2】

実施例	化 学 組 成 式
11	CaO · Al ₂ O ₃ · 0.012 SiO ₂ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 CeO ₂
比較11	CaO · Al ₂ O ₃ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 CeO ₂
12	CaO · Al ₂ O ₃ · 0.008 SiO ₂ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.0006 Pr ₆ O ₁₁
比較12	CaO · Al ₂ O ₃ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.0006 Pr ₆ O ₁₁
13	CaO · Al ₂ O ₃ · 0.012 SiO ₂ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 Gd ₂ O ₃
比較13	CaO · Al ₂ O ₃ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 Gd ₂ O ₃
14	CaO · Al ₂ O ₃ · 0.012 SiO ₂ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 Er ₂ O ₃
比較14	CaO · Al ₂ O ₃ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 Er ₂ O ₃
15	CaO · Al ₂ O ₃ · 0.012 SiO ₂ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 Tm ₂ O ₃
比較15	CaO · Al ₂ O ₃ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 Tm ₂ O ₃
16	CaO · Al ₂ O ₃ · 0.012 SiO ₂ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 Lu ₂ O ₃
比較16	CaO · Al ₂ O ₃ · 0.02 B ₂ O ₃ · 0.004 Eu ₂ O ₃ · 0.002 Nd ₂ O ₃ · 0.002 Lu ₂ O ₃

【0029】

【実施例17】

SrCO, 14.39 g

Al₂O₃, 14.95 gSiO₂, 0.02 gGeO₂, 0.02 gLi₂CO₃, 0.02 gH₃BO₃, 0.30 gEu₂O₃, 0.12 gDy₂O₃, 0.14 g

上記の配合組成の原料を十分混合し、97N₂+3H₂の混合ガス気流中で1400°Cで2時間焼成し、化学組成式SrO · 1.50Al₂O₃ · 0.003SiO₂ · 0.002GeO₂ · 0.003Li₂O · 0.025B₂O₃ · 0.004Eu₂O₃ · 0.004Dy₂O₃になる蓄光性蛍光体を得た。図6に励起停止10分後の発光スペクトルを示す。波長490nm付近にピークを持つ発

光特性を有することがわかる。目視で青緑の発光が観察され、しかも暗所において24時間以上残光が認識できた。

【0030】

【実施例18】

SrCO, 8.39 g

Al₂O₃, 5.80 gGeO₂, 0.24 gH₃BO₃, 0.14 gEu₂O₃, 0.20 gDy₂O₃, 0.22 g

上記の配合組成の原料を十分混合し、97N₂+3H₂の混合ガス気流中で1350°Cで2時間焼成し、化学組成式SrO · Al₂O₃ · 0.04GeO₂ · 0.020B₂O₃ · 0.010Eu₂O₃ · 0.010Dy₂O₃になる蓄光性蛍光体を得た。図7に励起停止10分後の発光スペクトルを示す。波長515nm付近にピークを持つ発

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光特性を有することがわかる。目視で黄緑の発光が観察され、しかも暗所において、24時間以上残光が認識できた。図8に発光波長515nmにおける励起スペクトルを示す。可視域においても405nm付近にピークを持つ幅広い励起波長帯域を有することから、本発明による蓄光性蛍光体材料は可視光にも高感度であることがわかる。

【0031】

【実施例19】

MgO	1.86g
CaCO ₃	1.92g
Sr(NO ₃) ₂	12.99g
Al(OH) ₃	8.99g
SiO ₂	11.52g
Eu ₂ O ₃	0.81g
Dy ₂ O ₃	1.43g
Si(還元剤)	0.22g

上記の配合組成の原料を十分混合し、1500°Cで3時間溶融した後、鉄板上にキャストし、化学組成式0.36MgO・0.15CaO・0.49SrO・0.45Al₂O₃・1.58SiO₂・0.018Eu₂O₃・0.030Dy₂O₃を有するガラスを作製した。こうして得られたガラスについて97N₂+3H₂の混合ガス気流中で1150°Cで5時間熱処理することによってSrAl₂Si₂O₇結晶を含むガラスセラミックス製蓄光性蛍光体が得られた。これは図2に示すような発光特性を有し、目視で白色の発光が観察され、しかも暗所において24時間以上残光が認識できた。

【0032】

【実施例20】

MgO	1.17g
CaCO ₃	10.20g
Al(OH) ₃	6.82g
SiO ₂	11.36g
Eu ₂ O ₃	1.28g
Nd ₂ O ₃	1.23g
Si(還元剤)	0.31g

上記の配合組成の原料を十分混合し、1500°Cで3時間溶融した後、鉄板上にキャストし、化学組成式0.22MgO・0.78CaO・0.33Al₂O₃・1.53SiO₂・0.028Eu₂O₃・0.028Nd₂O₃なるガラスを作製した。こうして得られたガラスについて、97N₂+3H₂の混合ガス気流中で1100°Cで5時間熱処理することによってCaAl₂Si₂O₇結晶を含むガラスセラミックス製蓄光性蛍光体が得られた。図9に励起停止10分後の発光スペクトルを示す。波長450、485および545nm付近にピークを持つ発光特性を有することがわかる。また、目視で紫青の発光が観察され、しかも暗所において24時間以上でも残光が認識できた。

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【0033】実施例4～16および比較例について、残光輝度の測定を行った。残光輝度はD65光源を200ルクスの照度で4分間照射し、その後の残光を輝度計で測定したものである。表3は励起停止10分後において、比較例の残光輝度を100とした時の実施例4～10の残光輝度の相対強度をまとめたものである。表4は励起停止5分後において、比較例11～16の残光輝度をそれぞれ100とした時のそれぞれ対応した実施例11～16の残光輝度の相対強度をまとめたものである。表3と表4から、SiO₂を含有させた本発明の蓄光性蛍光体の残光輝度は、従来のアルミニ酸塩蓄光性蛍光体に比べて著しく向上していることが分かる。

【0034】

【表3】

実施例	相対残光強度
4	150
5	225
6	250
7	220
8	205
9	200
10	175
比較例	100

【0035】

【表4】

実施例	相対残光強度
11	115
比較11	100
12	200
比較12	100
13	130
比較13	100
14	110
比較14	100
15	225
比較15	100
16	140
比較16	100

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【0036】【耐光性試験】蓄光性蛍光体は直接太陽光にさらされて使用される場合が多いので、太陽光、特にその中に含まれる紫外線に対して耐久性が高くなければならない。そこで、発光塗料の耐光性の試験方法（JIS規格による）に従って、本発明の実施例で得られた蛍

光体について、300Wの水銀灯を用いた耐光性試験を行った。その結果、いずれの実施例においても残光輝度の低下は認められなかった。

【0037】

【発明の効果】以上、述べたように、化学組成式は $R\cdot a(AI, Ga)_xO\cdot b(Si, Ge)_yO_z\cdot cEu^{2+}\cdot dM^{3+}$ （但し、RはBa, Sr, Ca, Mg等のアルカリ土類金属およびZnからなる群から選ばれる少なくとも1種であり、Mは共賦活剤で、Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Luからなる群から選ばれる少なくとも1種である）で示され、これらの組成範囲が特定範囲を有した。本発明による蓄光性蛍光体は、従来のアルミニン酸塩蛍光体に比べて、より多彩な発光波長を有すると共に、長残光時間・高残光輝度を実現し、しかもガラスセラミックスとして、多様な形状に成形することも可能な、今までにない有用な蓄光性蛍光体を提供することができる。*

*【図面の簡単な説明】

【図1】実施例1のX線回折パターンである。

【図2】実施例1の光励起停止10分を経過した後の発光スペクトルである。

【図3】実施例2のX線回折パターン。

【図4】実施例2の光励起停止10分を経過した後の発光スペクトルである。

【図5】実施例6と比較例の光励起停止10分を経過した後の発光スペクトルである。

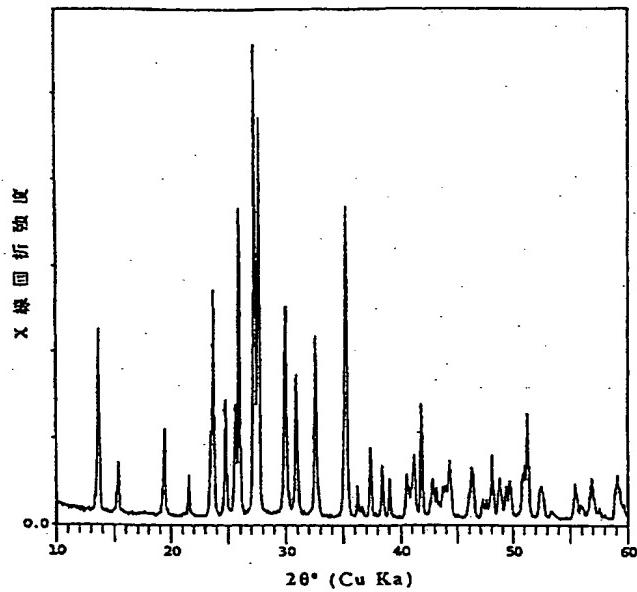
【図6】実施例17の光励起停止10分を経過した後の発光スペクトルである。

【図7】実施例18の光励起停止10分を経過した後の発光スペクトルである。

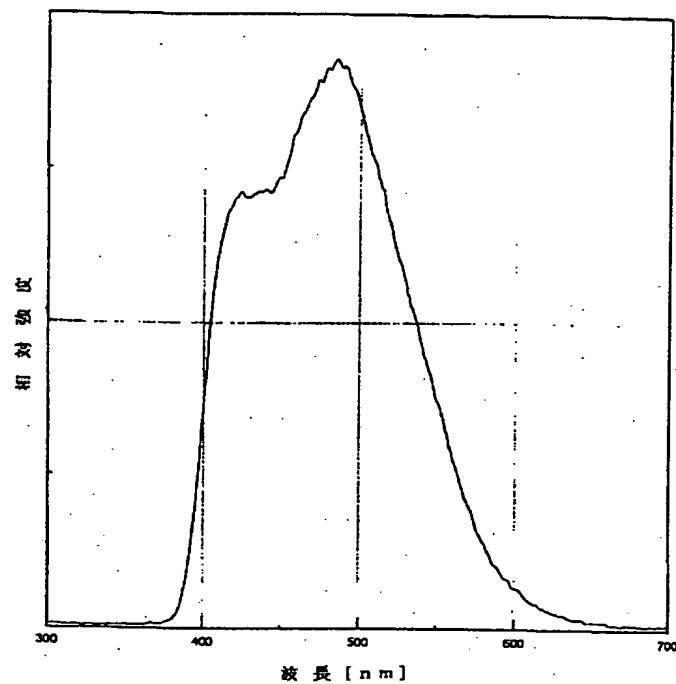
【図8】実施例18の発光波長515nmの励起スペクトルである。

【図9】実施例20の光励起停止10分を経過した後の発光スペクトルである。

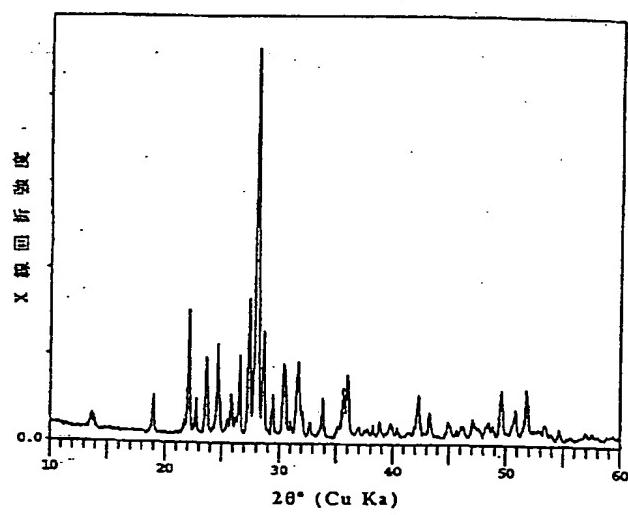
【図1】



【図2】



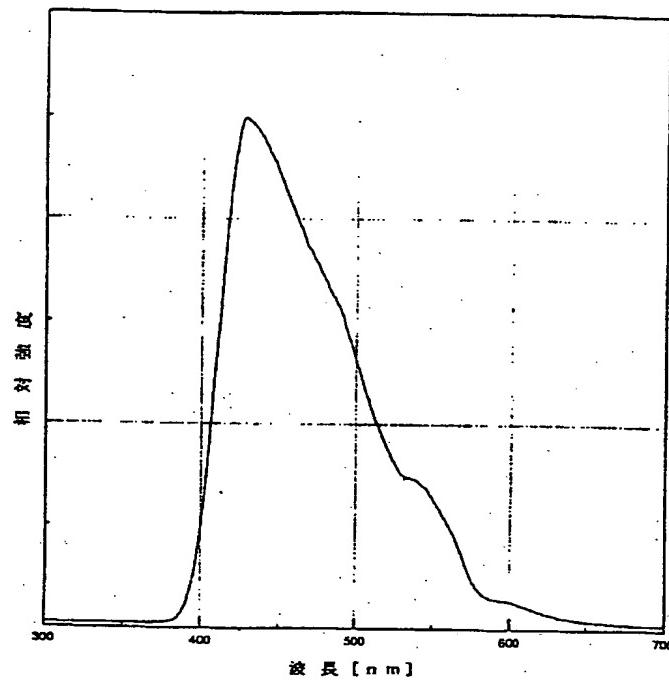
【図3】



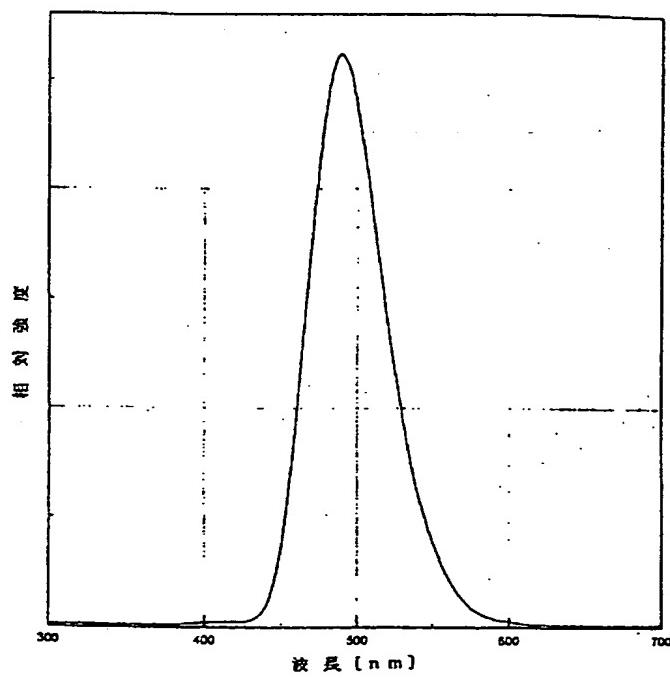
(10)

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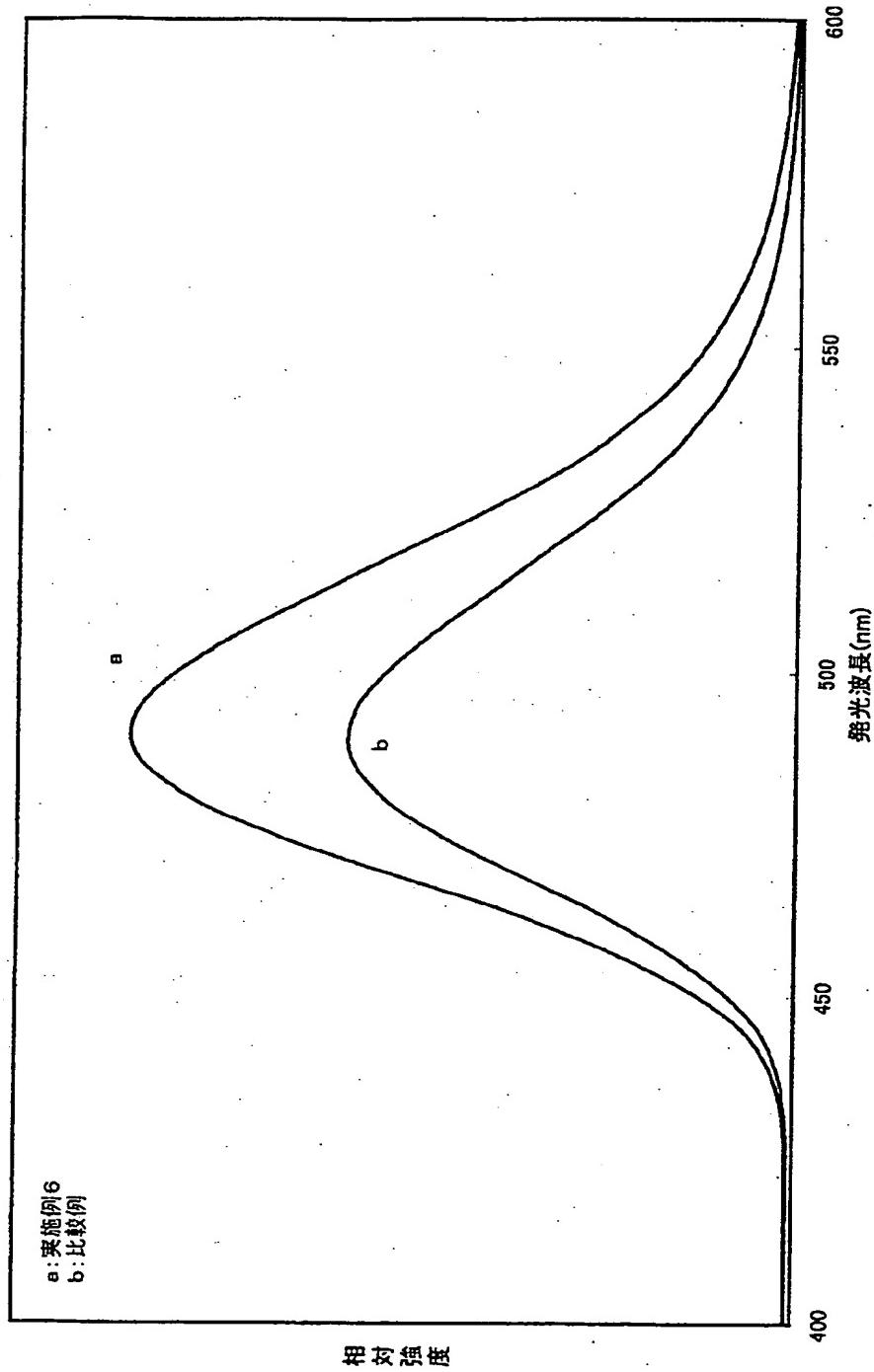
【図4】



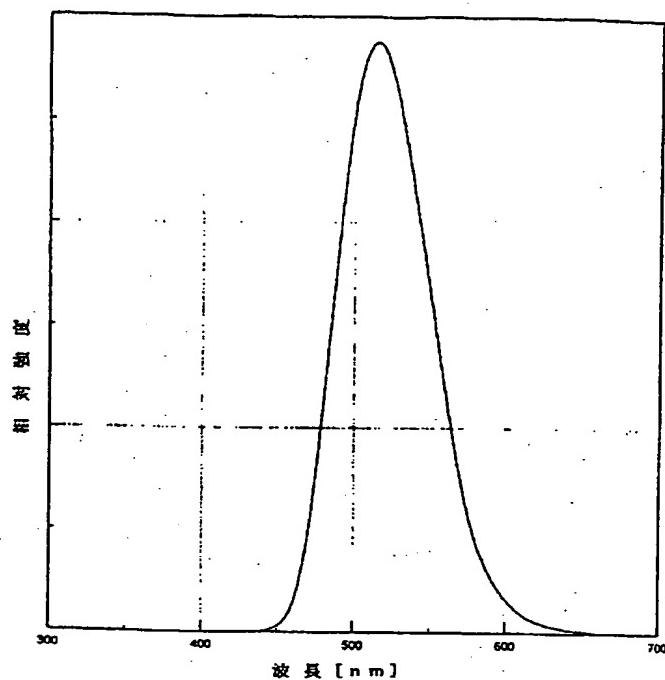
【図6】



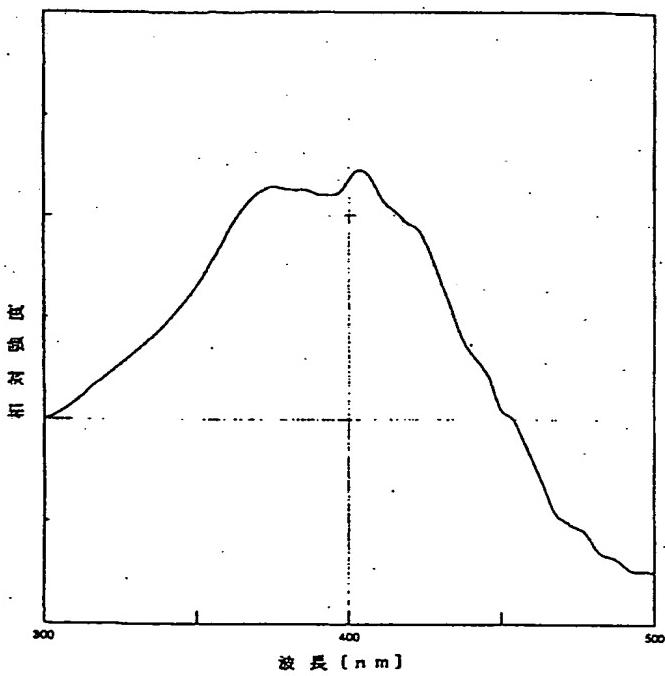
【図5】



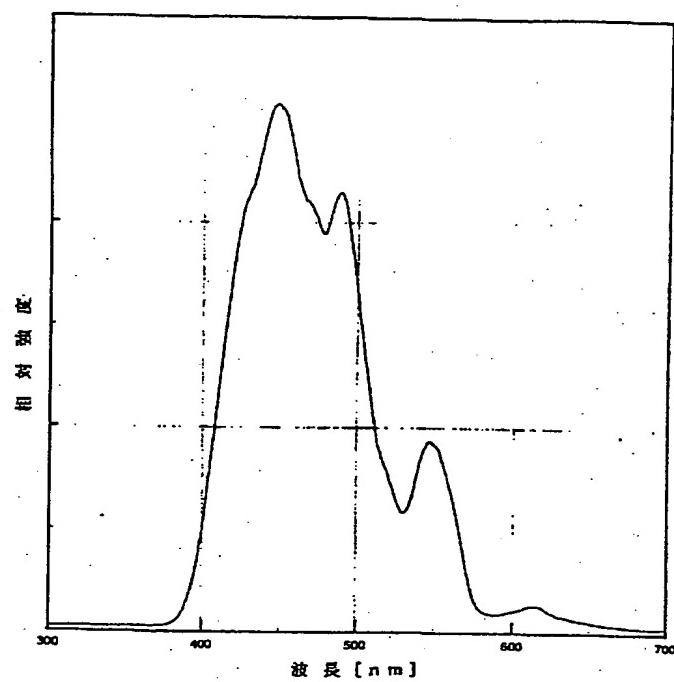
【図7】



【図8】



【図9】



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(54) PHOSPHORESCENT PHOSPHOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a phosphorescent phosphor which not only has long afterglow time and high afterglow brightness, but also can be used for obtaining a wide variety of gradations of color, and further for producing an article of such a complicated form that is difficult to manufacture from a conventional aluminate phosphor.

SOLUTION: This phosphorescent phosphor is activated by a divalent europium and the chemical composition is represented by the formula: $RO.a(Al_{1-x}Ga_x)_2O_3.b(Si_{1-y}Ge_y)O_2.cEu^{2+}.dM^{+}$, wherein R is at least one member selected from the group consisting of alkaline earth metals such as Ba, Sr, Ca, Mg and the like and Zn, and M is a coactivator and at least one member selected from the group consisting of Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, a, b, c, d, e, x and y being in ranges of $0.3 \leq a \leq 8.0$, $0.01 \leq b \leq 2.0$, $0.01 \leq c \leq 0.3$, $0.001 \leq d \leq 0.3$, $0 \leq x < 1.0$, $0 \leq y \leq 1.0$, respectively. A phosphorescent glass ceramics containing this phosphor is also provided.

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CLAIMS

[Claim(s)]

[Claim 1] Activation is carried out with divalent europium. The chemical composition type RO-a·(aluminum $1-x$ Gax) 2O3, b(Si $1-y$ Gey) O2, cEu $2+$, and Mn $+$ (However, R is at least one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, and M is a coactivator.) It is shown. at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu — it is — a, b, c, dx, and y are phosphorescent materials characterized by being in the range of $0.3 \leq a \leq 8$, $0.001 \leq b \leq 2$, $0.001 \leq c \leq 0.3$, $0.001 \leq d \leq 0.3$, $0 \leq x \leq 1.0$, and $0 \leq y \leq 1.0$, respectively.

[Claim 2] Phosphorescent fluorescence crystallized glass characterized by including a phosphorescent fluorescence crystal according to claim 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention Chemical composition type RO-a(aluminum $1-x$ Gax) 2O3, b (Si $1-y$ Gey) O2, cEu $2+$, anddMn $+$ (However, R is at least one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, and M is a coactivator.) It is shown at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sr, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu — it is — by long afterglow time amount and high afterglow brightness It is related with the crystallized glass containing new phosphorescent materials and this new with various luminescence wavelength.

[0002]

[Description of the Prior Art] the phenomenon in which, as for fluorescence, the matter emits the light near a visible range by the stimulus (excitation) from the outside — it is — a fluorescent lamp, a discharge lamp, and CRT (Cathode Ray Tube) — the so-called luminescence of the Braun tube etc. is this. Although the matter which emits fluorescence is called fluorescent substance, this is called phosphorescence when the fluorescence of the time amount (about 0.1 seconds) of extent sensed for an eye after an excitation halt continues. Moreover, the phosphorescence follows, i.e., afterglow time amount, reaches in several hours at a room temperature is called phosphorescent materials. About phosphorescent materials, two kinds, the sulfide represented by ZnS:Cu until now and the oxide which considered RAI 2O4 (R: alkaline earth metal) as the mother crystal, are reported. Although ZnS:Cu sulfide phosphorescent materials were put in practical use dozens of years ago, afterglow time amount has the trouble of being short in about at most 3 hours. Moreover, the decomposition reaction which becomes ZnS+H2 O→Zn+H2S produces these phosphorescent materials with the ultraviolet rays included in daylight, and the moisture contained in atmospheric air, the particle itself carries out melanism, and afterglow brightness falls gradually and has the ***** fault that an afterglow function fails remarkably for a short period of time. Therefore, this kind of phosphorescent materials were mainly limited to applications restricted dramatically, such as a watch with a luminous dial and indoor night display, the aluminate phosphorescent materials (U.S. Pat. No. 5376933, U.S. Pat. No. 5624008, and JP.8-73845,A —) which were developed on the other hand recently and by which activation was carried out by Eu $2+$ by considering RAI 2O4 as a mother crystal Since it has the property with it of JP.8-12772A, JP.8-151573A, and JP.8-151574A having afterglow time amount longer than ZnS:Cu, and moreover excellling also in chemistry endurance and lightfastness. In addition to applications, such as the existing watch with a luminous dial and an indoor night display, broad applications, such as a display, accessories, etc. of an accident prevention indicator and the safety for location recognition, are expected.

[Problem(s) to be Solved by the Invention] The further improvement in afterglow brightness and afterglow time amount is desired as the applicable field of phosphorescent materials is expanded.

[0004] Moreover, when using phosphorescent materials for accessories, such as a signboard, it is

desirable to use the afterglow of the most various possible color tones. Although it is indicated by above-mentioned JP.8-151573A that a color tone can be changed with the combination of an aluminate fluorescent substance, an activator, and a coactivator, the class of coactivator usable for change of a color tone is restricted to the range where change of the color tone which is limited, therefore is acquired is also comparatively narrow.

[0005] Furthermore, when using phosphorescent materials for accessories etc., it is wanted to offer the phosphorescent materials which are very difficult and solved this difficulty in the conventional aluminate phosphorescent materials which consist of a sintered compact to fabricate in the configuration of the tube of closing in with a thickness of 1mm or less.

[0006] This invention tends to offer the new phosphorescent materials which can obtain change of more various color tones in the luminescent color, being made in view of the trouble which said conventional aluminate phosphorescent materials have, and realizing long afterglow time amount and high afterglow brightness rather than the conventional thing. Moreover, this invention tends to offer new phosphorescent materials with able to manufacture the article of a difficult configuration manufacturing, if aluminate phosphorescent materials are used.

[0007] [Means for Solving the Problem] This invention doped Eu $2+$ as an activator, and a coactivator simultaneously for solution of the above-mentioned technical problem. A chemical composition type RO-aluminum $1-x$ Gax) 2O3, b(Si $1-y$ Gey) O2, cEu $2+$, anddMn $+$ (However, R is at least one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, and M is a coactivator.) at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu — it is — the new phosphorescent materials which consist of crystallized glass containing the crystal and this which are expressed are offered.

[0008] Many fluorescent substances are developed in the alkaline-earth-metal aluminum silicate which used Eu $2+$ as the activator until now. For example, in JP.47-41B, the fluorescent substance which consists of RO-aluminum2O3 and 2SiO2Eu (R: alkaline earth metal) is shown, and the fluorescent substance which consists of O-Al(Ba,CaxMg y Euz) 2O3 and bSiO2 is shown in JP.7-458561B at it. These fluorescent substances show the luminescence property from which the aluminate fluorescent substance which does not contain silicon differed. This is considered to originate in a host's ligand field. It is because luminescence of Eu $2+$ uses 4f-4f5d transition, so it is very easy to be influenced of the strength of the surrounding chemistry environment of Eu $2+$, i.e., the ligand field of the host who incorporates Eu $2+$. Although these alkaline-earth-metal aluminum silicate fluorescent substances have sufficient luminescence brightness needed for practical use, they were altogether developed a fluorescent lamp and for CRT, and its afterglow time amount is dramatically short. In the case of RO-aluminum2O3 and the 2SiO2:Eu fluorescent substance actually shown in JP.47-41B, it is indicated that afterglow time amount is remarkably short and a time constant is 1 or less microsecond. That is, these ingredients emit light, when irradiating light, but when an exposure is stopped, luminescence is the fluorescent substance which declines quickly and does not have afterglow nature.

[0009] Here, since ligand field are so strong that the electron density of coordination oxide ion, i.e., basicity, is high, fission of 5d orbit becomes large and luminescence initiation level energy falls, shifting fluorescence to a long wavelength side is known with the increment in basicity. Then, the alkaline-earth-metal aluminum silicate fluorescent substance used for a fluorescent lamp or CRT as a fluorescent substance which does not have the conventional afterglow nature is received. If high-persistence is realized by adding an effective coactivator in order to lengthen afterglow time amount Since it becomes possible to change the strength of a host's ligand field broadly by adjusting the ratio of aluminum2O3+Ga 2O3 and SiO2+GeO2 from which basicity differs mutually, it is expectable to acquire the luminescence property which is rich in change much more from the existing aluminate phosphorescent materials. Moreover, an alkaline-earth-metal aluminum silicate fluorescent substance After vitrifying, a chemical composition type by fusing and heat-treating RO-aluminum1-xGax) 2O3, b(Si $1-y$ Gey) O2, cEu $2+$, anddMn $+$ (However, R is at least one sort chosen from the group which consists of alkaline earth metal

and Zn, such as Ba, Sr, calcium, and Mg, and M is a coactivator.) It is possible to make it crystallized glass including the crystal which consists of being at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. In this way, if the fluorescent substance used as crystallized glass is used, a light-gage tube with a thickness of 1mm or less etc. can also fabricate easily the article of a configuration which was not able to be fabricated with the conventional sintered compact ceramics.

[0010] As a result of repeating research paying attention to an alkaline-earth-metal aluminum silicate fluorescent substance without the decay characteristic based on the above ideas, while introducing Eu²⁺ as an activator, and a coactivator, this invention person The presentation ratio of aluminum $2O_3+Ga\cdot2O_2$, the concentration of Eu²⁺, and the concentration of a coactivator within the limits of specification, respectively by selection combination *****. Compared with the conventional aluminum phosphorescent materials, it has a more variegated luminescence property, and by long afterglow time amount and high afterglow brightness, glass moreover also finds out possible phosphorescent materials, and it came to make this invention.

[0011] Namely, phosphorescent materials according to claim 1 Chemical composition type RO-a (aluminum $1-xGa\cdot x$) $2O_3$, b(Si $1-yGe\cdot y$) O_2 , cEu²⁺, anddMn⁺ (However, R is at least one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, and M is a coactivator.) It is shown, at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu — is — They are the phosphorescent materials characterized by a, b, c, dx, and y being in the range of $0.3 \leq a \leq -8$, $0.001 \leq -b \leq -2$, $0.001 \leq -c \leq 0.3$, $0.001 \leq d \leq -0.3$, $0 \leq x \leq 1.0$, and $0 \leq y \leq 1.0$, respectively. Invention according to claim 2 is phosphorescent fluorescence crystallized glass characterized by including a phosphorescent fluorescence crystal according to claim 1.

[0012] In the phosphorescent materials of this invention, a shows the presentation ratio of aluminum $2O_3$ or aluminum $2O_3$, and Ga $2O_3$, and b shows the presentation ratio of SiO 2 and/or GeO 2 . It influences mutually, respectively, and suits, and the strength of a host's ligand field changes by adjusting them, consequently a and b also change luminescence wavelength, afterglow brightness, and afterglow time amount. Afterglow brightness can be made high, if a is made small and b is enlarged, or if it enlarges a and b is made small. However, a limitation is located in the range, in the range of $0.3 \leq a \leq 8$, by b < 0.001, the effectiveness of Si and/or germanium is weak and b > 2 cannot obtain a fluorescent substance with high afterglow brightness. Moreover, in the range of $0.001 \leq -b \leq -2$, a fluorescent substance with high afterglow brightness cannot be obtained in range other than $0.3 \leq a \leq 8$, desirable — the range of $0.3 \leq a \leq 6$ and $0.001 \leq -b \leq -2$ — it is the range of $0.5 \leq a \leq 3$ and $0.002 \leq -b \leq -2$ especially preferably.

[0013] c must show the concentration of an activator and the range of it must be $0.001 \leq c \leq -0.3$.

Afterglow brightness to the extent that optical absorption can recognize bad in $c < 0.001$ with the naked eye is not obtained, but a lifting and afterglow brightness fall concentration quenching to reverse by $c > 0.3$ desirable — $0.001 \leq c \leq 0.2$ — it is the range of $0.002 \leq c \leq 0.1$ especially preferably.

[0014] d shows the concentration of a coactivator and the range of it is $0.001 \leq d \leq 0.3$. The afterglow brightness falls to reverse gradually by $d > 0.3$ desirable — $0.001 \leq d \leq 0.2$ — it is the range of $0.002 \leq d \leq 0.15$ especially preferably.

[0015] x can realize the fluorescent substance superior to conventional Zn:S:Cu in afterglow time amount and afterglow brightness also by showing the substitutional rate when permuting aluminum by Ga, and permuting a part of aluminum by Ga. In addition, although the permutation by Ga of aluminum is possible also for about 100% of permutation, if it is going to acquire said better property, the range of the range of $x \leq -0.5$ will be $x \leq 0.2$ desirable especially preferably.

[0016] y can realize the fluorescent substance superior to conventional Zn:S:Cu in afterglow time amount and afterglow brightness also by showing a substitutional rate in case germanium permutes Si, and permuting a part of Si by germanium. In addition, although the permutation by

germanium of Si is possible also for total replacement arthroplasty, if it is going to acquire said better property, the range of the range of $y \leq 0.5$ will be $y \leq 0.2$ desirable especially preferably.

[0017] Moreover, boric acid, Li $2CO_3$, LiCl, the Lynn system compound, etc. can be added as flux in the case of composition of the phosphorescent materials of this invention. The optimal addition is 0.05 ~ 8% of range in mol%.

[0018]

[Embodyment of the Invention] The phosphorescent materials of this invention are compoundable with the following sintering processes. After carrying out weighing capacity of the oxide which is the constituent of the phosphorescent materials of this invention, or the various compounds which can turn into an oxide by the pyrolysis and fully mixing them by the predetermined ratio, it puts into an alumina crucible and calcinates at 1100~1600 degrees C by reducing atmosphere for 1 to 10 hours. The baking object obtained depending on the presentation may be ground, and it may calcinate on the same conditions again.

[0019] Moreover, the phosphorescent materials of this invention are producible also by the manufacture approach of the crystallized glass described below. That is, after carrying out weighing capacity of the start raw material by the predetermined ratio and fully mixing, it puts into an alumina crucible and heating fusion is carried out at 1300~1600 degrees C according to reducing atmosphere for 1 to 3 hours. Then, the cast of the melting liquid is carried out on a gridde, and tabular glass is produced. In this way, by heat-treating the obtained glass by reducing atmosphere 950~1250 for 1 to 12 hours. Chemical composition type RO-(aluminum $1-xGa\cdot x$) $2O_3$, b(Si $1-yGe\cdot y$) O_2 , cEu²⁺, anddMn⁺ (However, R is at least one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, and M is a coactivator.) The phosphorescent materials made from crystallized glass including the crystal which consists of being at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu are obtained. It can fabricate in crystallized glass, then the sintered compact ceramics easily also with the product with which shaping carried out the configuration of the tube of difficult thin meat etc. Moreover, although sufficient reinforcement which the opening between the particles before sintering remained as a hole in a sintered compact, and suited the object on the application of a product may not be obtained with the ceramics by the sintering process, since what precise and uniform without such a hole is obtained in crystallized glass, the product which is superior to the sintered compact ceramics in reinforcement is obtained. Thus, the thing of the form which is not acquired with a sintering process can also be realized, and it is expected that application worth of phosphorescent materials of this invention increases further.

[0020]

[Example] Hereafter, although a concrete example explains this invention, this invention is not limited only to these examples.

[0021]

[Example 1]

Sr CO_3 5.69gAl(s) 203 3.93gSiO (s) 2 4.63gH $3BO_3$ 0.19gEu(s) 203 0.27g (ies) 203 The raw material of a combination presentation of 0.29g above was mixed enough, it calcinated at 1350 degrees C in the mixed-gas air current of $9N_2+3H_2$ for 2 hours, and the phosphorescent materials used as chemical composition type SrO-aluminum $2O_3$ -2.00SiO 2 -0.04 B-2O 3 , 0.020Eu $2O_3$, and 0.020Dy 203 were obtained. In the analysis of the X diffraction pattern shown in drawing 1, it became clear that these phosphorescent materials consist of 20SiAl $2Si_3$ phase. The emission spectrum 10 minutes after an excitation halt is shown in drawing 2. It turns out that it has a peak wavelength of 420nm, and near 483nm, and has the luminescence property which is not looked at by the conventional phosphorescent materials. Moreover, white luminescence was observed and viewing has also recognized afterglow in a dark place for 24 hours or more.

[0022]

[Example 2]

Ca CO_3 4.42gAl(s) 3 (OH) 6.90gSiO (s) 2 5.30gH $3BO_3$ 0.22gEu(s) 203 0.19gNd(s) 203 The raw material of a combination presentation of 0.36g above was mixed enough, it calcinated at 1350

degrees C in the mixed-gas air current of 97N2+3H2 for 2 hours, and the phosphorescent materials set to chemical composition type CaO-aluminum203-2.00SiO2-0.04 B-2O3, 0.012Eu2O3, and 0.024Nd2O3 were obtained. In the analysis of the X diffraction pattern shown in drawing 3, it became clear that these phosphorescent materials consist of 20CaAl2Si8 phase. The emission spectrum 10 minutes after an excitation halt is shown in drawing 4. It turns out that an emission spectrum consists of a big luminescence peak near the wavelength of 425nm, and a small luminescence peak near 540nm unlike the conventional thing. Moreover, visually, luminescence of a purple-blue color was observed and afterglow has been recognized in a dark place for 24 hours or more.

[0023]

[Example 3]
 $\text{CaCO}_3 \cdot 4.3\text{gAl} \cdot 203 \cdot 4.27\text{gGa(s)} \cdot 203 \cdot 0.20\text{gSiO(s)} \cdot 2 \cdot 4.45\text{gNH}_4\text{H}_2\text{PO}_4 \cdot 1.76\text{gEu(s)} \cdot 203 \cdot 0.18\text{gNd(s)}$
 203 Mix enough the raw material of a combination presentation of 0.34g above, and it calcinates at 1350 degrees C in the mixed-gas air current of 97N2+3H2 for 2 hours. The phosphorescent materials set to chemical composition type CaO and 0.95aluminum203-1.6SiO2-0.02Ga2O3-0.17P2O5, 0.012Eu2O3, and 0.022Nd2O3 were obtained. Thus, the obtained fluorescent substance consists of 20CaAl2Si8 phase, and it has a luminescence property as shown in drawing 4. Moreover, visually, luminescence of a purple-blue color was observed and afterglow has been recognized in a dark place for 24 hours or more.

[0024]

[Example 4]
 $\text{CaCO}_3 \cdot 7.17\text{gAl(s)} \cdot 203 \cdot 7.25\text{gSiO(s)} \cdot 2 \cdot 0.025\text{gH}_3\text{BO}_3 \cdot 0.18\text{gEu(s)} \cdot 203 \cdot 0.15\text{gNd(s)}$
 203 Mix enough the raw material of a combination presentation of 0.23g above, and it calcinates at 1350 degrees C in the mixed-gas air current of 97N2+3H2 for 2 hours. The phosphorescent materials which serve as CaO-aluminum203, 0.005SiO2-0.02 B-2O3, 0.006Eu2O3, and 0.012Nd2O3 by the chemistry chemical composition formula were obtained. Thus, the obtained fluorescent substance had a luminescence peak in the wavelength of 440nm, visually, luminescence of a purple-blue color was observed and, moreover, afterglow has been recognized in a dark place for 24 hours or more.

[0025] An example 4, the examples 5-10 which show the same luminescent color by the same approach, and the example of a comparison which does not contain SiO2 were produced. A table 1 summarizes the presentation of 4-10. The emission spectrum of the example 6 10 minutes after an excitation halt and the example of a comparison is shown in drawing 5. It turns out that the phosphorescent materials of this invention emit light more strongly. Moreover, the fluorescent substance of these examples has recognized afterglow in a dark place for 24 hours or more.

[0026]

[A table 1]

実施例	化 学 組 成 式
4	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.005 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.006 \text{Eu}_2\text{O}_3 \cdot 0.012 \text{Nd}_2\text{O}_3$
5	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.009 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.006 \text{Eu}_2\text{O}_3 \cdot 0.012 \text{Nd}_2\text{O}_3$
6	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.014 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.006 \text{Eu}_2\text{O}_3 \cdot 0.012 \text{Nd}_2\text{O}_3$
7	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.028 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.006 \text{Eu}_2\text{O}_3 \cdot 0.012 \text{Nd}_2\text{O}_3$
8	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.036 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.006 \text{Eu}_2\text{O}_3 \cdot 0.012 \text{Nd}_2\text{O}_3$
9	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.040 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.006 \text{Eu}_2\text{O}_3 \cdot 0.012 \text{Nd}_2\text{O}_3$
10	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.048 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.006 \text{Eu}_2\text{O}_3 \cdot 0.012 \text{Nd}_2\text{O}_3$
比較例	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.006 \text{Eu}_2\text{O}_3 \cdot 0.012 \text{Nd}_2\text{O}_3$

[0027] Moreover, about the example of a comparison corresponding to the examples 11-16 and each example which added Ce, Pr, Gd, Er, Tm, and Lu with Coactivator Nd (what "the comparison" attached before the number), it produced by the same approach as an example 4, and those chemical composition types were summarized in a table 2. [A table 2]

[A table 2]

実施例	化 学 組 成 式
11	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.012 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.002 \text{CeO}_3$
比較11	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.002 \text{CeO}_3$
12	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.008 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.0006 \text{Pr}_2\text{O}_3$
比較12	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.0006 \text{Pr}_2\text{O}_3 \cdot 0.002 \text{Gd}_2\text{O}_3$
比較13	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.002 \text{Gd}_2\text{O}_3 \cdot 0.002 \text{Er}_2\text{O}_3$
14	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.012 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.002 \text{Er}_2\text{O}_3$
比較14	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.002 \text{Br}_2\text{O}_3 \cdot 0.002 \text{Tm}_2\text{O}_3$
15	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.012 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.002 \text{Br}_2\text{O}_3$
比較15	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.002 \text{Tm}_2\text{O}_3$
16	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.012 \text{SiO}_2 \cdot 0.02 \text{B}_2\text{O}_3 \cdot 0.004 \text{Eu}_2\text{O}_3 \cdot 0.002 \text{Nd}_2\text{O}_3 \cdot 0.002 \text{Lu}_2\text{O}_3$

[A table 2]

[Example 17]
 $\text{SrCO}_3 \cdot 14.39\text{gAl(s)} \cdot 203 \cdot 14.95\text{gSiO(s)} \cdot 2 \cdot 0.02\text{gGeO(s)} \cdot 2 \cdot 0.02\text{gH}_3\text{BO}_3 \cdot 0.30\text{gEu(s)} \cdot 203 \cdot 0.12\text{gD(ies)} \cdot 203$ Mix enough the raw material of a combination presentation of 0.14g above, and it calcinates at 1400 degrees C in the mixed-gas air current of 97N2+3H2 for 2 hours. The phosphorescent materials set to chemical composition type SrO, 1.50aluminum203, 0.003SiO2, 0.002GeO2, 0.003Li2O, 0.025 B-2O3, 0.004Eu2O3, and 0.004Dy2O3 were obtained. The emission spectrum 10 minutes after an excitation halt is shown in drawing 6. It turns out that it has the luminescence property which has a peak near the wavelength of 490nm. Visually, bluish green luminescence was observed and, moreover, afterglow has been recognized in a dark place for 24 hours or more.

[0030]

[Example 18]

$\text{SrCO}_3 \cdot 8.39\text{gAl} \cdot 203 \cdot 5.80\text{gGeO(s)}_2 \cdot 0.24\text{gH}_3\text{BO}_3 \cdot 0.14\text{gEu(s)}$ 203 0.20gD (ies) 203 The raw material of a combination presentation of 0.22g above was mixed enough, it calcinated at 1350 degrees C in the mixed-gas air current of 97N₂+3H₂ for 2 hours, and the phosphorescent materials set to chemical composition type SrO-aluminum2O₃-0.04GeO₂, 0.020 B-203, 0.010Eu2O₃, and 0.010Dy 203 were obtained. The emission spectrum 10 minutes after an excitation halt is shown in drawing 7. It turns out that it has the luminescence property which has a peak near the wavelength of 515nm. Visually yellow-green luminescence was observed and, moreover, afterglow has been recognized in a dark place for 24 hours or more. The excitation spectrum in the luminescence wavelength of 515nm is shown in drawing 8. Since it has the broad excitation wavelength band which has a peak near 405nm also in a visible range, it turns out that the phosphorescent-materials ingredient by this invention is high sensitivity also at the light.

[0031]

[Example 19]

$\text{MgO} \cdot 1.86\text{gCaCO(s)}_3 \cdot 1.92\text{gSr(s)}_2 \cdot (\text{NO3})_3 \cdot 12.99\text{gAl(s)}_3 \cdot (\text{OH}) \cdot 8.99\text{gSiO(s)}_2 \cdot 11.52\text{gEu(s)}$ 203 0.81gD (ies) 203 1.43gSi(s) (reducing agent) After mixing enough the raw material of a combination presentation of 0.22g above and fusing at 1500 degrees C for 3 hours. The cast was carried out on the gridle and the glass which has chemical composition type 0.36MgO, 0.15CaO, 0.49SrO, 0.45aluminum2O₃-1.58SiO₂, 0.018Eu2O₃, and 0.030Dy 203 was produced. In this way, the phosphorescent materials made from crystallized glass including 203SrAl2Si₈ crystal were obtained by heat-treating at 1150 degrees C in the mixed-gas air current of 97N₂+3H₂ about the obtained glass for 5 hours. This had the luminescence property as shown in drawing 2, and visually, white luminescence was observed and, moreover, it has recognized afterglow in a dark place for 24 hours or more.

[0032]

[Example 20]

$\text{MgO} \cdot 1.7\text{gCaCO(s)}_3 \cdot 10.20\text{gAl(s)}_3 \cdot (\text{OH}) \cdot 6.82\text{gSiO(s)}_2 \cdot 11.30\text{gEu(s)}$ 203 1.28Nd(s) 203 1.23gSi(s) (reducing agent) the gridle top after mixing enough the raw material of a combination presentation of 0.31g above and fusing at 1500 degrees C for 3 hours — the cast — carrying out — chemical composition type 0.22MgO, 0.78CaO, 0.33aluminum2O₃-1.53SiO₂, 0.028Eu2O₃, and 0.028Nd 203 — glass was produced. In this way, the phosphorescent materials made from crystallized glass which include 203CaAl2Si₈ crystal about the obtained glass by heat-treating at 1100 degrees C in the mixed-gas air current of 97N₂+3H₂ for 5 hours were obtained. The emission spectrum 10 minutes after an excitation halt is shown in drawing 9. It turns out that it has the luminescence property which has a peak wavelength 450,405 and near 545nm. Moreover, visually, luminescence of purple/blue was observed and afterglow has been recognized in a dark place for at least 24 hours or more.

[0033] Afterglow brightness was measured about examples 4-16 and the example of a comparison. Afterglow brightness irradiates the D65 light source for 4 minutes with the illuminance of 200 lux, and measures subsequent afterglow with a luminance meter. A table 3 summarizes the relative intensity of the afterglow brightness of the examples 11-16 to which it corresponded, respectively when setting the afterglow brightness of the examples 11-18 of a comparison to 100 after [of an excitation halt] 10 minutes. A table 4 summarizes the relative intensity of the afterglow brightness of the examples 11-18 to which it corresponded, respectively when setting the afterglow brightness of the examples 11-18 of a comparison to 100 after [of an excitation halt] 5 minutes, respectively. A table 3 and a table 4 show that the afterglow brightness of the phosphorescent materials of this invention which made SiO₂ contain is improving remarkably compared with the conventional aluminate phosphorescent materials.

[0034]

[A table 3]

実施例	相対蛍光強度
4	1.50
5	2.25
6	2.50
7	2.20
8	2.05
9	2.00
10	1.76
比較例	1.00

[0035] [A table 4]
[Effect of the Invention]

実施例	相対蛍光強度
1.1	1.16
比較例1	1.00
1.2	2.00
比較例2	1.00
1.3	1.30
比較例3	1.00
1.4	1.10
比較例4	1.00
1.5	2.25
比較例5	1.00
1.6	1.40
比較例6	1.00

[0036] Since [radiationproofing test] phosphorescent materials are used in many cases, being exposed to direct sunlight, its endurance must be high to sunlight and the ultraviolet rays included especially in it. Then, according to the test method (based on JIS) of the lightfastness of a luminous paint, the radiationproofing test which used the mercury-vapor lamp of 300W was performed about the fluorescent substance obtained in the example of this invention. Consequently, lowering of afterglow brightness was not accepted in which example.

[0037] [Effect of the Invention] As stated, a chemical composition type As mentioned above, RO-a (aluminum1-xGa)x 2O3, b(Si1-yGey) O2, cEu²⁺, andMn²⁺ (However, R is at least one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, and M is a coactivator.) It is shown, at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu — it is — These presentation range the phosphorescent materials by this invention with the specific range While having more variegated luminescence wavelength compared with the conventional aluminate fluorescent substance, long afterglow time amount and high afterglow brightness can be realized, and the useful phosphorescent materials which can moreover also be fabricated in various configurations as crystallized glass and which are not until now can be offered.

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the X diffraction pattern of an example 1.

[Drawing 2] It is the emission spectrum after optical-pumping half 10 minutes of an example 1 pass.

[Drawing 3] The X diffraction pattern of an example 2.

[Drawing 4] It is the emission spectrum after optical-pumping half 10 minutes of an example 2 pass.

[Drawing 5] It is the emission spectrum after optical-pumping half 10 minutes of an example 6 and the example of a comparison pass.

[Drawing 6] It is the emission spectrum after optical-pumping half 10 minutes of an example 17 pass.

[Drawing 7] It is the emission spectrum after optical-pumping half 10 minutes of an example 18 pass.

[Drawing 8] It is an excitation spectrum with a luminescence wavelength [of an example 18] of 515nm.

[Drawing 9] It is the emission spectrum after optical-pumping half 10 minutes of an example 20 pass.

[Translation done.]